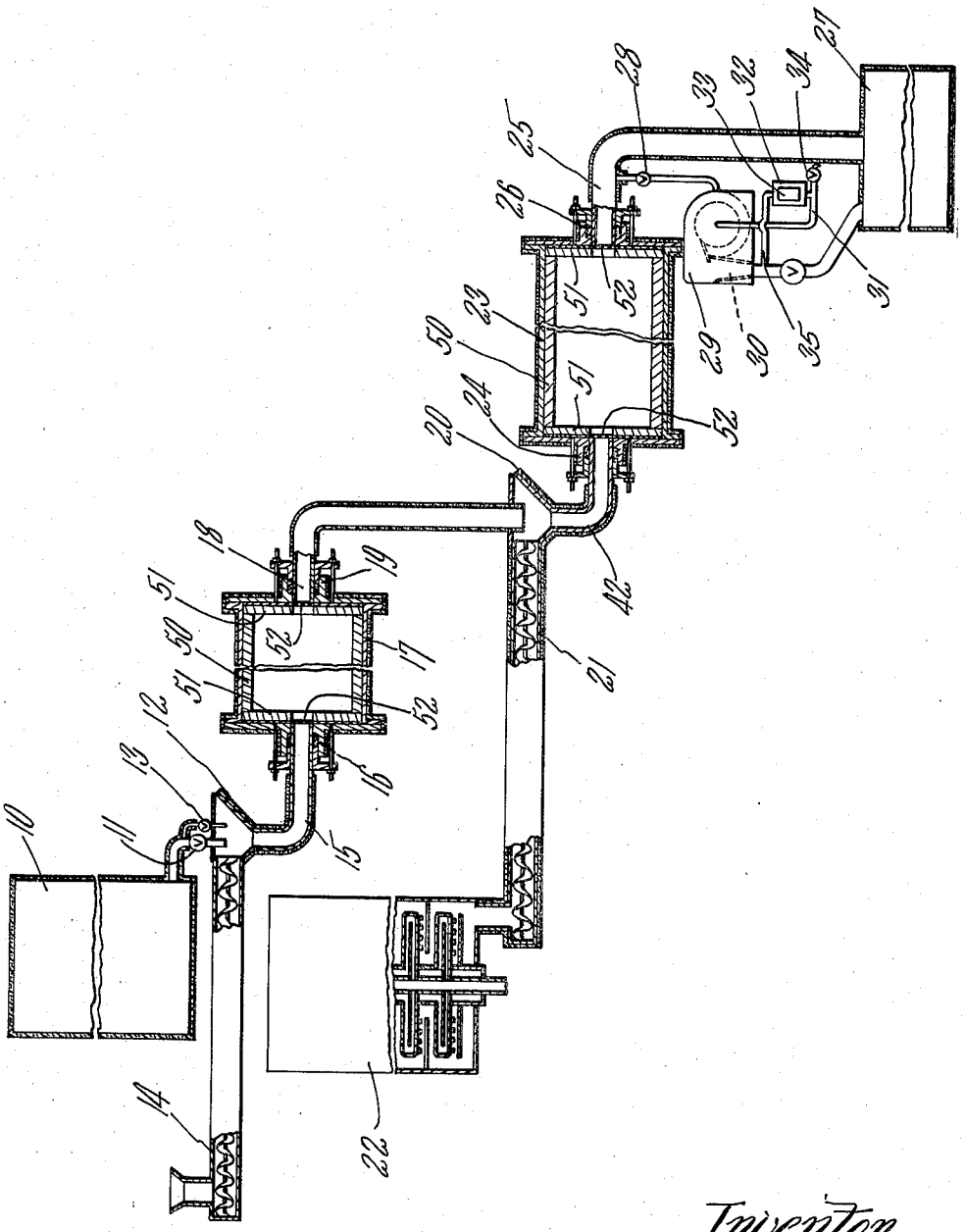
June 27, 1939. H. K. MOORE 2,164,141

CAUSTICIZATION OF SOLUBLE SULPHIDES

Filed June 23, 1936



Inventor
Hugh K. Moore
by Wright, Brown, Quinby & May
Attys

Patented June 27, 1939 2,164,141

UNITED STATES PATENT OFFICE

2,164,141

CAUSTICIZATION OF SOLUBLE SULPHIDES

Hugh Kelsea Moore, York Harbor, Maine, assignor to Brown Company, Berlin, N. H., a corporation of Maine

Application June 23, 1936, Serial No. 86,765

2 Claims. (Cl. 23—185)

This invention relates to the causticization of solutions of soluble sulphides, such as sodium sulphide, potassium sulphide, barium sulphide, and strontium sulphide. I shall describe my invention in terms of the causticization of sodium sulphide solutions, but what I shall say in this regard applies generally to potassium sulphide, barium sulphide, and strontium sulphide solutions. Accordingly, it should be understood that in the following description and in the appended claims I regard solutions of potassium sulphide, barium sulphide, and strontium sulphide as being the chemical equivalents of solutions of sodium sulphide. More specifically, the present invention devolves about improvements of the practices described in my application Serial No. 670,882, now Patent No. 2,056,929, dated October 6, 1936, filed May 13, 1933, which, along with other phases of invention, deals with the causticization of solutions of soluble sulphides.

In the aforementioned patent application, I have described the production of sodium sulphide solutions containing not only sodium monosulphide but sodium polysulphides. I have further described the desirability of reducing substantially all of the sodium polysulphides in solution to the monosulphide stage preparatory to the causticization of the solutions with cupric oxide, as it is only the sodium monosulphide that can be causticized with cupric oxide substantially without undesirable side reactions. Such reduction of the sodium polysulphides in solution may be readily accomplished with finely divided heavy elemental metal, copper being cited as the preferred heavy element metal for this purpose. Once the sulphides in solution have been reduced substantially in entirety to the monosulphide stage, the solution may be causticized with the cupric oxide while keeping side-reaction products at a minimum. As further pointed out in that application, causticization is performed to best advantage with what has been termed therein as activated cupric oxide. The mode of activating the cupric oxide disclosed in that application is to subject a slurry of the cupric oxide to the abrading and/or pounding action of a suitable instrumentality, such as a ball mill. The slurry of activated cupric oxide so produced is then added to the solution of substantially only sodium monosulphide to effect the desired causticizing reaction thereupon.

In practicing the causticizing reaction as disclosed in the aforementioned application, it is necessary to add activated cupric oxide to the sodium monosulphide solution in an amount greatly above that theoretically necessary to ensure a complete causticization of the sodium sulphide in solution, as the cupric oxide particles acquire a crust or coating of cupric sulphide which prevents the particles of cupric oxide from being completely consumed in the causticizing reaction. Moreover, it is necessary for the operator to take samples of liquor from the causticizing tanks for the purpose of testing the extent to which causticization has gone and thus to ensure a final liquor substantially completely rid of sulphide. Because of the considerable time that elapses between the operator's taking samples of liquor from the causticizing tanks and his reaching a conclusion that causticization has gone to the desired end-point, there is serious danger that the causticized liquor may remain in contact with the unconsumed or excess cupric oxide for an undesirably long period of time sufficient to give rise to reaction between the caustic soda and the cupric oxide to form undesirable complex soluble copper compounds as impurities that must be removed from the solution in order to arrive at finished caustic soda of the desired salable quality. In other words, once the causticizing reaction has gone to the desired end-point, it is undesirable that the caustic soda solution be in contact with cupric oxide particles, for even though these particles may be crusted or coated with protective cupric sulphide, yet there is progressive penetration of caustic soda solution to the interiors or cores of the particles with attendant formation of a slight amount of undesirable complex soluble copper compounds. It is thus seen that the causticizing operation disclosed in my aforementioned patent application must be carefully controlled with a view toward avoiding undue standing of the causticized solution in contact with residual or unconsumed cupric oxide. Once soluble cupric compounds have crept into the solution as impurities, soluble iron compounds are also apt to get thereinto as impurities, for the iron apparatus with which the causticized solution contacts tends to acquire copper as a deposit while it is displacing copper from solution in accordance with the well-known principle that iron, because of its greater electro-potential, will displace copper from a solution of copper compounds. Accordingly, it is seen that provision has to be made for the elimination of iron as well as copper impurities from the causticized solution.

The present invention is designed to obviate difficulties of the foregoing kind that arise in the causticization of sodium monosulphide solutions with cupric oxide. Generally stated, the present

invention provides for the commingling with the cupric oxide of substantially only that amount of sodium monosulphide in solution that can be theoretically causticized by the cupric oxide under conditions ensuring a substantially complete causticization of the sodium monosulphide. It is thus seen that the resulting causticized solution is without excess or unconsumed cupric oxide, wherefore, there is no danger of contaminating the solution with soluble copper compounds and/or iron compounds and there is no need for careful supervision of the causticizing reaction.

With the foregoing and other features and objects in view, I shall now describe my invention in detail with reference to the accompanying drawing, which illustrates more or less diagrammatically and conventionally apparatus that I may advantageously employ.

Before describing the apparatus, the reactions effected therein, and the principles employed in operating the apparatus, I deem it desirable to make some general observations about the materials of construction of the apparatus. An important quality desired in the apparatus is that it shall not react with the solution at any point in the system. For this purpose, I have found it desirable to employ pipes, pumps, tanks, agitators, etc., which are nickel-clad wherever solution makes contact therewith, as nickel is not chemically affected by the solution either when it contains sodium sulphide and/or caustic soda. In this connection, it might be noted that nickel-clad steel sheets are available on the market in a form fabricated by rolling comparatively thin nickel plate onto steel plate of comparatively much greater thickness affording the desired strong backing and together with the nickel constituting a unitary laminated structure.

For the purpose of the present invention, let us assume that one starts with a solution of sodium monosulphide and sodium polysulphides produced, for instance, as disclosed in my aforementioned patent application. Such a solution may be delivered to and maintained in a storage tank **10**, from which a stream of solution may be progressively withdrawn through a valved outlet pipe **11** discharging into a funnel-shaped receiver **12**. It is desriable that the rate at which solution is withdrawn from the tank **10** be closely regulated so that, as shown, a small valved bleed pipe **13** leads off from the pipe **11** above the valve of the latter and also discharges into the receiver **12**. By adjusting the valves of both pipes, it is possible to regulate closely the rate of withdrawal of solution from the tank **10**. It is, of course, possible and preferable to withdraw solution continuously and accurately at the desired rate from the tank **10** by means of so-called dosers, but the manner of feeding illustrated has been chosen for sake of simplicity. The stream of sodium sulphide solution continuously entering the receiver **12** washes over finely divided metallic copper also being fed into the receiver in regulated amount by a worm conveyor **14**. The stream carries the copper downwardly therewith through a pipe **15** which serves to conduct the slurry through a packing gland **16** forming part of an inlet end header of a rotary ball mill **17** wherein the desulphurization of the polysulphides in solution to the monosulphide stage is being effected. The amount of finely divided metallic copper used for this purpose is sufficient to do the work of desulphurization, but this amount need be much less than that used according to the aforementioned patent application, since the ball mill scours or rubs the surfaces of the particles of copper so as to expose clean metallic copper for the desulphurizing reaction. The ball mill shoud be one whose lining and whose balls consist of substantially pure copper so as to avoid fouling of the solution with the material of construction of the ball mill. As appears in the drawing, the lining **50** consists of a comparatively thick cylindrical copper shell which, when it becomes worn by use, may be readily removed as a unit and renewed. To this end, the ball mill may also comprise end copper lining plates **51** which, along with the cylindrical copper shell **50**, may be removed by unfastening the end headers and their associated packing glands. In between each end lining plate and the corresponding header is shown a centrally perforated plate **52** whose perforations are sufficiently large to permit ready passage therethrough of solution and finely divided solids but of sufficiently restricted size to keep the balls of the ball mill from escaping therethrough even after such balls have become so decidedly worn or reduced in size as to be practically inutile and thus require replacement.

A stream of solution containing substantially only sodium monosulphide dissolved therein and containing elemental copper and copper sulphide suspended therein leaves the ball mill through an exit pipe **18** encompassed by a stuffing box **19** forming part of an exit end header of the ball mill. The stream discharges into a funnel-shaped receiver **20** and washes over cupric oxide also being delivered into the receiver by a worm **21**, which gets such copper oxide from a suitable roasting furnace **22**, for instance, a Hirschoff furnace, constantly producing cupric oxide from copper sulphide. The copper sulphide being roasted in the furnace is that recovered from the desulphurizing and causticizing operations, as will presently appear. At this point, it is well to observe that the volume of sodium monosulphide solution constantly being delivered into the receiver **20** is carefully regulated so as to bring into contact with the cupric oxide an amount of sodium sulphide substantially equal to that theoretically capable of being causticized by the cupric oxide. It is preferable that there be an extremely slight excess of cupric oxide for a reason presently to be explained. The stream of solution delivered into the receiver **20** carries along therewith the cupric oxide designed to do the work of causticization through a pipe **42** entering into a second rotary ball mill **23** by way of a stuffing box **24** forming part of the inlet end header of the mill. The ball mill **23** is preferably lined and otherwise constructed similarly to the ball mill **17**. It should be noted that the stream constantly running into the ball mill **23** is a solution of substantially only sodium monosulphide containing suspended therein not only the cupric oxide that is to serve as the causticizing reagent but also the copper sulphide and the unconsumed metallic copper emerging from the ball mill **17**. The ball mill **23** should also be one whose lining and balls consist of substantially pure copper so as to avoid contaminating the solution with the material of construction of the ball mill. I have found that by carrying out the causticizing reaction in such a ball mill, it is possible to effect a virtually instantaneous and substantially complete causticization of the sodium sulphide solution with no more cupric oxide than is theoretically necessary for such purpose, wherefore, such troubles as are encountered in the aforementioned patent application may be com-

pletely avoided. Evidently the rubbing and pounding action of the copper balls in the ball mill is such as to expose constantly fresh surfaces of cupric oxide for causticizing action on the sodium sulphide, there being little, if any, opportunity for a crust or coating of cupric sulphide to form on the cupric oxide particles. It is evidently the case that the abrading and pounding action of the copper balls, besides constantly exposing fresh surfaces of copper oxide or comminuting the copper oxide to finer particle size, drives water into the cupric oxide to activate it for the causticizing reaction, the effect probably being that of developing incipient cupric hydroxide. This latter explanation is the only one of which I can conceive that comports with the surprising activity imparted to the copper oxide for causticizing the sodium monosulphide, for, the cupric oxide as delivered by the roasting furnace **22** is of comparatively very slow reactivity for causticizing the sodium sulphide solution. Indeed, the copper oxide as delivered by the roasting furnace **22** cannot, even when allotted a comparatively long causticizing period, react to completion with the sodium sulphide solution. On the other hand, the activated copper oxide produced hereby reacts almost instantaneously and in substantially theoretically calculated amount or molecular equivalent with the sodium monosulphide solution to causticize the latter. Here is the way the causticizing reaction that takes place in the ball mill **23** may be written:

$$CuO+Na_2S+H_2O=CuS+2NaOH$$

It is doubtful whether the reaction actually takes place in the foregoing manner. Probably a number of reactions take place, as follows:

1. $Na_2S+H_2O=NaHS+NaOH$
2. $CuO+H_2O=Cu(OH)_2$
3. $Cu(OH)_2+NaHS=CuS+NaOH+H_2O$

In other words, it is probable that the sodium hydrosulphide into which sodium sulphide hydrolyzes in water, according to the first equation, reacts with the cupric hydroxide produced in water, according to the second equation, to yield cupric sulphide and sodium hydroxide, as indicated by the third equation.

The causticized solution constantly flows out of the ball mill **23** by way of a discharge pipe **25** surrounded by a stuffing box **26** forming part of the exit end header of the mill. The causticized solution containing cupric sulphide and metallic copper in suspension therein may be run into a storage tank **27**, whence it may be delivered to a separator, such as a Dorr classifier and/or filter (not shown), designed to remove the suspended solids thereupon as a substantially dewatered sludge. The sludge may be sent to the roasting furnace **22** wherein both the copper sulphide and metallic copper may be converted into cupric oxide for reuse in the causticizing reaction, as hereinbefore described. The causticized solution may be concentrated to the desired degree for sale in any one of the forms of caustic soda of commerce, as disclosed in my aforementioned application.

In order to make certain that the causticizing reaction in the ball mill **23** is taking place properly, that is, with substantial theoretical exactness, it is preferable that the discharge pipe **25** be equipped with a tiny bleed pipe **28** which serves to deliver constantly a sample of the causticized liquor to a miniature rotary or continuous filter **29** directly therebelow. The filter functions to eliminate the copper sulphide and metallic copper from the causticized solution and to discharge the sludge through a valved hopper member **30** and the filtered liquor through a pipe **31**. Such removal by filtration or otherwise of substantially all the solids suspended in the test-stream of solution bled off from the main stream of causticized solution is desirable in ascertaining, through the color displayed by such stream, the end-point of the causticizing reaction. In this connection, it will be appreciated that because of the presence of residual metallic copper and precipitated copper sulphide in the test-stream, it presents a black or inky appearance that makes color-inspection of such stream practically impossible. However, by first practically completely removing from such test-stream the solids suspended therein, the true or intrinsic color of the solution becomes open to inspection by view through the proper sort of inspecting or sight-chamber so as to enable an accurate determination of the end-point of the causticizing reaction, as will presently appear. To this end, the pipe **31** may be led through a trap **32** of comparatively large cross-sectional area equipped with both front and back windows **33** of substantial thickness and substantial freedom from color. An intense white light may be projected from a suitable electric lamp or other source (not shown) through the back window so that an operator stationed in front of the front window may visually examine the color of the liquor in the trap **32**. As already indicated, it is preferable to use a very slight excess of cupric oxide beyond that theoretically necessary for causticizing the sodium sulphide in solution. Under normal conditions of operation, that is, when the sodium sulphide solution is being substantially completely causticized, this exceedingly slight excess of cupric oxide will impart a faint blue tinge to the causticized liquor, which faint tinge is readily observable by the operator when he looks through the comparatively deep layer or large volume of solution constantly being maintained in the trap **32**. When any blue tinge is exhibited by the causticized solution, the operator is positively assured that there is no sodium sulphide whatever left in the solution. The depth of blue exhibited by the causticized solution in the trap **32** serves as a guide to the operator, enabling him to adjust the flow of sodium sulphide solution from the tank **10** to the ball mill **17**. Thus, should the causticized solution exhibit a blue tinge in excess of the faintest blue detectable by the operator, he is immediately apprised of the fact that he is not running sufficient sodium sulphide solution from the tank **10** into the ball mill **17**, and, accordingly, he increases the flow of the solution until the faintest blue tinge detectable is produced in the trap **32**. On the other hand, should the operator observe that the liquor in the trap **32** is of a yellow hue or is without hue of any kind, he knows at once that a superfluity of sodium sulphide solution is being run into the ball mill **17** and, accordingly, he immediately reduces the volume of flow of solution into the ball mill **17** to a degree such that he gets the desired faintest blue hue in the trap **32** that he can detect.

As an additional check on his power of observation, the operator may take off a drop or two of the liquor running through the pipe **31** on a spot-plate and add to such drop or drops a bit of silver nitrate solution. If, after standing, the drop of liquor treated with the silver nitrate solu-

tion develops no brown or black coloration, the operator knows beyond peradventure that there is no sodium sulphide whatever present in the causticized liquor. To enable the operator to take off drop samples of liquor, the pipe **31** is shown equipped with a tiny cock **34**. The test liquor coming out of the trap **32** may, of course, be joined with the batch proper in the tank **27**; and, so, too, the filtered solids or sludge from the hopper **30** may be joined with the batch proper in the tank **27**. Preferably, as illustrated, the stream of liquor issuing from the trap **32** is caused to flow through a pipe **35** into the hopper **30** wherein it is commingled with the filtered solids or sludge so that the sludge may be washed out of the hopper and the mixture be delivered to the batch proper in the tank **27**.

There are various advantages in the practice of the present invention hereinabove outlined, chief of which are substantial foolproofness of operation, saving in labor costs, and elimination of equipment and supervision otherwise necessary. It might be observed that cupric oxide in excess of that necessary to do the work of causticization tends to accumulate in the system, since the metallic copper used in the desulphurizing reaction is added to the copper sulphide formed during causticization and the mixture converted into copper oxide. Accordingly, cupric oxide should be progressively removed from the roasting furnace and cupric sulphide should be progressively removed from the sludge on its way to the roasting furnace, the two commingled, and the mixture roasted, as disclosed in my aforementioned application, to produce metallic copper for reuse in the desulphurizing reaction, the amount of metallic copper thus produced being substantially only that necessary for the desulphurizing reaction in the ball mill **17** so as to maintain a substantial constancy of cupric oxide for the causticizing reaction in the ball mill **23**. In producing such metallic copper, substantially pure sulphur dioxide gas results as a by-product, as disclosed in my aforementioned application. An economical cyclic process wherein only mechanical losses of chemical need be made up is thus afforded by the practice of the present invention. The solution of caustic soda produced by the practice of the present invention contains the merest traces of soluble copper salts as an impurity; and these may be very easily and economically removed by electrolysis.

There are other noteworthy features of the invention hereof. Thus, it is distinctly preferable to lag with suitable heat-insulating material the various instrumentalities through which flow of the materials being processed hereby takes place. It is for this reason that the drawing shows an outside layer of insulation on practically all of the instrumentalities, although the worm conveyer **14** has not been shown so insulated by reason of the fact that the metallic copper being conveyed thereby is in cold condition; and the roasting furnace **22** is not shown so insulated by reason of the fact that it is impractical so to do under the excessively high temperatures at which such furnace is operated. By thus conserving the heat in the solution being processed, the solution may be maintained at higher chemical concentration with no crystallization, such as might otherwise obtain; and reaction thereon is promoted by virtue of the higher temperature preserved therein for reaction. Again, it should be noted that the cylindrical shells forming part of the conveyors **14** and **21** are preferably composed of, or lined with, copper so as to avoid contaminating the solution with undesirable metallic or other impurities. However, it may be preferable to construct the worm conveyors themselves of stainless steel because of the great toughness and hardness of such steel, which may advantageously be a stainless steel alloy of the type containing a high percentage of chromium and nickel and characterized by the quality of acquiring greater toughness and hardness as it undergoes abrasion and other stress. Of course, it is possible to use a copper worm of appropriate structure, a worm constructed of nickel, "Monel" metal, or a nickel-plated steel or copper worm.

The process hereof has been described in terms of using finely divided elemental copper for desulphurizing the polysulphides associated with the sulphide solution to be causticized and also in terms of using cupric oxide as the causticizing reagent for the resulting monosulphide solution, as copper and copper oxide present important economic advantages. However, it is to be understood that the process hereof might be conducted with the equivalents of copper and copper oxide, for instance, such heavy elemental metal as silver and such heavy metal oxide as silver oxide. Other heavy elemental metals or heavy metal oxides, although possible of use herein, present disadvantages, for instance, that of forming undesirable side reaction products in comparatively larger amount. Again, while the desulphurization of the original sulphide solution to the monosulphide stage in the presence of elemental copper has been described as being effected in a ball mill whose surfaces exposed to the solution are composed of copper and while the causticization of the resulting monosulphide solution has been described as being effected in the presence of cupric oxide in a ball mill whose surfaces exposed to the monosulphide solution are composed of copper, it is to be understood that instrumentalities which effect an abrading and pounding action might be used in lieu of a ball mill, for instance, such machines as hammer-mills, rod mills, eccentric roller mills, stamp mills, colloid mills, homogenizers, etc. In such latter case, too, it is distinctly desirable that the surfaces of the machine coming in contact with the solution be composed of copper. Accordingly, in using the term "ball mill" in the appended claims, it is to be understood that the term means a ball mill and/or its various equivalents.

It is well to note some other advantages of the process hereof. An important advantage of the process hereof over that of my application Serial No. 670,882 now Patent No. 2,056,929, is the utilization of the heat content of the hot copper oxide as it comes directly from the roasting furnace and is commingled with the monosulphide solution in concentrating the solution and raising its temperature so as to promote the causticizing reaction to be effected thereupon. In the case of my earlier-filed application, according to which the activation of the copper oxide is performed in water and the activated aqueous slurry commingled with the monosulphide solution, not only is the heat originally present in the copper oxide lost or dissipated, but the water associated with the slurry causes undesirable dilution of the monosulphide solution. Another important aspect of the process hereof is that the amount of copper in the system is comparatively small, the copper being recycled many times in a comparatively short period and thus enabling large caustic soda production for a

given amount of copper. It is thus possible to maintain the copper inventory in the process hereof comparatively low and thus avoid what might otherwise be a substantial capital investment. The process hereof is further easy to conduct continuously with low labor costs, since the progressive flow or feed of materials through the system with accurate control of the finished caustic soda solution can be had merely by regulating the valve or valves through which the original sulphide solution passes into the system. The process hereof thus does away with such operations as handling, weighing, and analyzing the copper oxide and/or measuring and analyzing the contents of the various tanks in the system.

I claim:

1. A process of causticizing an alkali metal monosulphide solution with copper oxide, which comprises continuously and simultaneously feeding a stream of monosulphide solution and a stream of finely divided copper oxide into a mixing and reacting chamber while subjecting said copper oxide in contact with such solution in the chamber to abrading and pounding action, thereby promoting practically immediate and complete causticizing reaction by the copper oxide on a chemical equivalent of sulphide in solution, continuously emitting from the chamber as a stream the causticized solution continuously being formed therein, and controlling the rate of feed of the stream of monosulphide solution relative to the rate of feed of the stream of finely divided copper oxide into the chamber to ensure a continuous emission from the chamber of a causticized solution substantially free from dissolved sulphide and copper constituents.

2. A process of causticizing an alkali metal monosulphide solution with copper oxide, which comprises continuously and simultaneously feeding a stream of monosulphide solution and a stream of finely divided copper oxide into a mixing and reacting chamber while subjecting said copper oxide in contact with such solution in the chamber to abrading and pounding action, thereby promoting practically immediate and complete causticizing reaction by the copper oxide on a chemical equivalent of sulphide in solution, continuously emitting from the chamber as a stream the causticized solution and copper sulphide produced by said causticizing reaction, continuously bleeding off a test-stream from the stream of causticized solution emitted from said chamber, progressively removing the solids in suspension in said test-stream, progressively passing the resulting substantially clear test-stream through an illuminated sight-chamber adapted to display the color of said test-stream, and controlling the rate of feed of the stream of monosulphide solution relative to the rate of feed of the stream of finely divided copper oxide into the mixing and reacting chamber to cause said sight-chamber to display only a faint blue tinge in said test-stream, thereby ensuring the emission from said mixing and reacting chamber of a causticized solution substantially free from dissolved sulphide and containing only a slight trace of dissolved copper.

HUGH KELSEA MOORE.